CHAPTER 2
SURVEY OF LITERATURE

2.1 INTRODUCTION

Many researchers have developed and characterized copper sulphide thin films owing to their wide range of applications in numerous fields. Survey on the previous work and the ongoing work helps to know the present status of the material. In this chapter survey of copper sulphide material on various methods of preparation, its structural, optical, electrical and other properties has been carried out.

Gill and Bube (1970) have studied photovoltaic properties of Cu$_2$S/CdS hetero junctions before and after heat treatment using I-V characteristics, junction capacitance, and spectral response measurements. After heat treatment slow transients in the photo response and effects of secondary illumination were investigated. Many cells which had poor characteristics generally showed improved I-V characteristics after heat treatment. This heat treatment leads to a decreased junction capacitance, indicating the formation of narrow region of highly compensated CdS at the Cu$_2$S/CdS interface.

Changes in the photo-capacitance of the film before and after heat treatment have been studied by Lindquist et al (1972). The influence of trapped charge on the photovoltaic properties of an efficient Cu$_2$S-CdS single-crystal hetero junction has been studied by photo capacitance
technique. The trapped holes enhanced the 100 K photocurrent spectrum uniformly by a factor of 3 before heat treatment. After 200°C heat treatment in air, the maximum trapped charge at 100 K enhanced the photocurrent by two orders of magnitude.

Resistivity analysis of Cu$_2$S films has been done by Couve et al (1973) using vacuum evaporation method. Composition of the film has been measured by electrochemical method and it varies from $x=1.8$ to 2. They reported that resistivity increases as deviation from stoichiometric composition($x$) increases which may be due to compensation effect arising from unknown donors introduced during evaporation. Band gap energy of the film seems to be associated more with resistivity of the film than with the composition of $x$.

Kimihiko Okamoto et al (1973) have studied the conductivity measurement on compositions ranging from Cu$_{1.8}$S to Cu$_2$S and indium-doped Cu$_{1.8}$S. Conductivity increases as the deviation from stoichiometry increases and it was reported that digenite and djurilite undergo phase transition at 90 and 93°C respectively.

Gaustavino et al (1975) studied the electrical conductivity of hexagonal to digenite. They reported that conductivity decreases with increase in temperature for all films, except for stoichiometric sample, conductivity increases with increase in temperature.

Kazinets et al (1977) obtained Cu$_{1.8}$ S composition by vacuum evaporation method and reported that a slight depletion in the sulphur content of the samples results in increase in fcc lattice constant during evaporation. Furthermore, Cu$_{2-x}$S films have been prepared from individual component of copper and sulphur by Kazinets et al(1980). Different substrate temperature leads to phase transformation in the film which was due to gradual enrichment
of copper caused by partial volatilization of sulphur during treatment in vacuum.

Nimura et al (1977) reported that composition of evaporated \( \text{Cu}_2\text{S} \) and \( \text{Cu}_{1.8}\text{S} \) thin film varies with the distance between source and substrate and with the angle of incidence of vapor on substrate. The films with (\( \sigma \)) less than \( 10^1 (\Omega \text{ cm})^{-1} \) contain precipitations of Cu. The result show that the films with low conductivities are chalcocite and the films with conductivities in the order of \( 10^2-10^3 (\Omega \text{ cm})^{-1} \) consist of djurleite and digenite.

Relationship between thickness and stoichiometry of \( \text{Cu}_2\text{S} \) film has been studied by Hadley and Tseng (1977) using electrochemical techniques. It was reported that \( \text{CdS}/\text{Cu}_2\text{S} \) hetero junction solar cells have led to significant improvements in conversion efficiency.

Das et al (1978) have prepared \( \text{Cu}_{1.8} \) S films by a solid state reaction between \( \text{CdS} \) and \( \text{CuCl} \) films in the temperature range 200–250\(^0\) C. Results show that microstructure of \( \text{Cu}_2\text{S} \) film replicates the structure of \( \text{CdS} \) film. The grain size and surface topology of \( \text{Cu}_2\text{S} \) film are essentially the same as that of \( \text{CdS} \) film.

Loferski et al (1979) studied the cathode luminescence characteristics of \( \text{Cu}_x\text{S} \) films produced by sulfurization of copper and by chemical substitution of copper ions for cadmium ions in \( \text{CdS} \). Result shows that two distinct phases, chalcocite and tetragonal phase exist in cathode luminescence spectrum. The composition range for chalcocite at room temperature is \( \text{Cu}_{2.000}\text{S} \) to \( \text{Cu}_{1.996} \) S. The tetragonal phase in \( \text{Cu} \text{S} \) films produced by sulfurization of thin Cu films appears to exist in the range \( \text{Cu}_{1.96}\text{S} \) to \( \text{Cu}_{1.90}\text{S} \). Moreover, CL spectrum of pure chalcocite consists of a single band with its peak at about 0.96 \( \mu \text{m} \) and for tetragonal phase the peak consists of single band at about 0.91 \( \mu \text{m} \).
Rezig et al (1979) have used vacuum evaporation technique to prepare Cu$_x$S thin films. Result shows that resistivity of the film increases when the stoichiometry of Cu$_x$S changes from sulfur rich phase to copper rich phase during evaporation.

Armantrout et al (1979) have prepared Cu$_x$S film by sputtering copper in the atmosphere of H$_2$S and argon. Lean atmosphere of partial pressure of H$_2$S, results in the formation of cones and high resistivity whereas, increase in flow of pressure results in the disappearance of cone and decrease in resistivity.

Cu$_x$S film has been deposited by reactive sputtering using Ar-H$_2$S as a source by Arthur Jonath et al (1979). Films prepared at 135$^0$C substrate temperature show high resistivity and exhibit transition breakpoint at (103-106$^0$C) whereas, films prepared at room temperature show low resistivity and exhibit transition breakpoint at (96-101$^0$C).

Arjona et al (1979) have prepared Cu$_x$S thin films on hot glass substrate by two methods, a) sulphuration of copper film in a solution of thiourea, and b) vacuum evaporation of synthetic copper sulphide and condensation. The results obtained indicate that films prepared by thiourea sulphuration present a weak Hall effect due to the very low mobility charge carriers whereas, the films obtained by vacuum evaporation have higher value of charge carriers.

Rastogi and Salkalachen (1982) prepared Cu$_x$S film by vacuum evaporation method at different substrate temperatures. Results show that the films prepared at low substrate temperature exhibit stoichiometric composition, whereas high substrate temperature film exhibits deviation in the stoichiometry of the film.
Wagner and Wiemhofer (1983) prepared Cu$_x$S thin films with different stoichiometric compositions by two different techniques (i) evaporation of Cu$_x$S and (ii) reactive sputtering from a Cu target in an Ar-H$_2$S-H, atmosphere on glass substrates. Result show that increase in the values of the Hall mobility from 2 to 3, corresponds to stoichiometric composition of Cu$_x$S in the vicinity of $x = 2$.

Chopra et al (1983) had analyzed theoretically the solar cell efficiency of copper sulphide hetero junction, and reported that the Cu$_2$S/CdS were capable of achieving practical conversion efficiencies of above 10% whereas; Cu$_2$S/ZnCdS have conversion efficiencies of 9%.

Joy George and Joseph (1984) prepared copper sulphide thin films by relatively evaporating copper and sulphur. XRD studies indicate that grains are oriented with (001) planes perpendicular to substrate surface.

Eddy Vanhoecke et al (1984) synthesized Cu$_2$S film on glass substrate by sputtering method with copper as target and Ar-H$_2$S mixture as sputtering gas and the sputtered film corresponds to 004, 008, 012 orientation. Results reveal that change in the H$_2$S pressure results in change in the composition of copper-sulphur phases. Moreover slight deviation in the composition causes a drastic change in the resistivity of the film.

Fatas et al (1985) have used CuSO$_4$ and thiourea in alkaline medium to deposit Cu$_x$S thin films by chemical method. They reported that optical band gap and resistivity of the film is of the order of 2.58 eV and $3 \times 10^{-3} \Omega \text{ cm}$, respectively.

Gadgil et al (1986) prepared Cu$_2$S films onto glass and aluminum substrates using the flash evaporation technique. The film deposited onto aluminum showed higher value of solar absorptance with a thermal emittance
of 0.20. Thermal emittance of the film increased as the temperature increases from 100 to 250°C. Films coated on glass substrates show low values of thermal emittance, thereby indicating the presence of intrinsic selective properties. The films deposited on glass possess excellent conducting properties.

Varkey (1989) deposited Cu$_x$S using EDTA as a complexing agent in a bath comprising CuCl, NaCl and hydroxylamine hydrochloride solutions. It was reported that the as-grown films and the films annealed in air are highly conductive in nature with low resistivity. The high conductivity of the film was due to nonstoichiometry of the film that results from Cu vacancies and hole concentration. Increase in resistivity has been reported for the films annealed in H$_2$ and annealing the films in N$_2$ does not vary resistivity appreciably. The conductivity mechanism in Cu$_x$S films is governed by several factors such as impurity, stoichiometry, deposition techniques and conditions. However, it was concluded that doping with Cd reduces resistivity fluctuations associated with temperature variations.

Nair et al (1991) prepared Cu$_x$S thin films from chemical bath constituted from copper (II) nitrate or chloride, NH$_3$(aq), NaOH, triethanolamine and thiourea for application as solar control coatings and for architectural glazing. At ambient temperature (25°C), the duration of deposition ranges from 2 to 12 hr, but at 50°C, deposition was considerably faster; from 1 to 2 hr 50 min. Cu$_x$S films deposited in this manner require air annealing at 150°C for about 10 min, to reduce the integrated infrared transmittance, to about 10%. The optical transmittance spectra of the annealed films are peaked in the 0.55-0.575 μm wavelength range, which provide a greenish yellow illumination inside the building under daylight that corresponds to the peak in the spectral sensitivity curve of the human eye for phototropic (daylight) vision. The reduction in the sheet resistance of Cu$_x$S
films with air annealing, ensures a low thermal emittance which is a requirement for high-efficiency solar control coatings. Nair et al (1991) showed the possibility of obtaining optimized Cu$_x$S thin film on glass substrates using chemical bath deposition method. They reported the optoelectronic and solar control applications of chemically deposited Cu$_x$S thin films. Nair and Nair (1991) have reported that absorption greater than 90% can be observed in chemically deposited SnS–Cu$_x$S thin films. These films have wide applications in glass evacuated tube solar collectors.

Ivan Grozdanov and Metodija Najdoski (1995) studied four kinds of Cu$_x$S thin films of different composition such as Cu$_2$S, Cu$_{1.8}$S, Cu$_{1.4}$S and CuS on glass and metal substrates deposited by electroless chemical deposition from aqueous copper thio-sulphate baths in acidic media. Optical properties of the film reveal that Cu$_2$S thin film shows high transmission throughout the spectral region, whereas CuS films were found to be highly absorptive in the near infrared region.

Cristina Nagcu et al (1997) deposited CuS thin films by spray pyrolysis technique using aqueous solutions containing CuCl, .2H$_2$O, thiourea and cationic surfactant for different substrate temperatures between 150 and 210°C. It was explained that the higher the substrate temperature, the greater would be the optical clarity of the film. The optical transmission spectra of CuS films indicate that the transmission decreases with increasing film thickness, mainly because of the increase in crystallite size of the film. Transmission spectra of the films at different thicknesses vary in such a way that the transmission in the visible region becomes more remarkable, while at the same time a substantial decrease in transmission throughout the NIR region is observed.
Lindroos et al (2000) have prepared copper sulphide thin films by successive ionic layer adsorption and reaction method at room temperature. The films were polycrystalline and showed no preferred orientation.

Sartale and Lokhande (2000) deposited Cu$_x$S thin films by successive ionic layer adsorption and reaction (SILAR) method using copper sulphate and thiourea solutions as cationic and anionic precursors. The films were deposited on glass and Si wafer substrates. Preparative conditions such as concentration, pH and temperature of cationic and anionic precursor solutions adsorption, reaction and rinsing time durations etc, were optimized during preparation. The film prepared on glass substrate consists of fine grains, whereas increase in crystallinity was observed for the films prepared on Si wafer substrate.

Cruz-Vazquez et al(2000) reported amorphous CuS films supported on polyethylene substrate that are treated with iodine and alkali metal iodides in organic solvents. The electrical conductivity of the film exhibits metal-like temperature dependence down at 120K, while untreated films had a minimum resistance at 250 K. Upon treatment with I$_2$, a major part of CuS was converted to CuI, and the co-existence of two chemical species enhanced electrical conduction.

He et al (2001) have prepared Cu$_2$S and CuS film on glass substrate using reactive RF sputtering method with optimized parameters such as power, temperature of the substrate and gas flow of H$_2$S. XRD studies show that Cu$_2$S films have (002) orientation and both compounds have same hexagonal structure.

Surface and electrical properties of thin Cu$_x$S films grown on different substrates (polyethylene and micro-porous-Si layer) are investigated by Setkus et al (2001). It was reported that increasing amount of copper
hydroxide and copper sulfate results in extreme decrease of sensitivity to ammonia at room temperature.

Pathan et al (2002) prepared Cu$_2$S film by using modified chemical method. The preparative conditions such as concentration, complextant, reaction and rinsing time durations were optimized to get stoichiometric Cu$_2$S film. They reported that resistivity decreases with an increase in temperature which indicates semi-conducting nature of Cu$_2$S film. Optical properties reveal that Cu$_2$S film exhibits high absorbance with increased conductivity of the film.

Cu$_2$S films were deposited by cathodic electro-deposition in the presence of Ethylenediaminetetraacetate (EDTA) in aqueous solution on Ti substrate by Anuar et al(2002). Results reveal that films prepared at higher concentration of CuSO$_4$ show poor conductivity.

Johansson et al (2002) deposited copper sulfide thin films on soda lime glass and Si(100) substrates by Atomic Layer Deposition (ALD) using β-diketonate-type volatile Cu compound Cu(thd)$_2$ and H$_2$S as precursors. Depositions were carried out in the temperature range 125–250 °C on glass and silicon substrates, growth rate being approximately 0.3 Å cycle$^{-1}$ on both substrates of films of thickness above 50 nm. For lower thickness films the growth rate was higher, approximately 0.5 Å cycle$^{-1}$.

Svetlana Erokhina et al (2002) formed CuS nanoparticles by exposing deposited LB films of copper stearate to the H$_2$S atmosphere for at least 12 hr. The aggregation of the nanoparticles into thin layers was performed by washing the sample with chloroform after the reaction for removing stearic acid molecules. The dependence of electrical conductivity upon frequency was reported for CuS layers of different thicknesses. The
electrical conductivity was found to depend strongly on frequency when the thickness of the precursor copper stearate LB films is less than 30 bilayer.

Sheng-Yue Wang et al (2003) deposited $\text{Cu}_x\text{S}$ ($x=1, 2$) thin films by asynchronous-pulse ultrasonic spray pyrolysis (APUSP) technique on glass from $\text{CuCl}_2$ and thiourea at relatively low temperature without any complexing agent. The deposited films close to CuS were found to be polycrystalline phases, while $\text{Cu}_2\text{S}$ films exhibit mixture of amorphous and polycrystalline as well. The result show that the crystallite phase of particles highly depends on molar ratio of thiourea to $\text{CuCl}_2$ and the pyrolysis temperature.

Jiban Podder et al (2005) deposited $\text{Cu}_x\text{S}$ thin films by photochemical method on indium–tin–oxide-coated glass substrates from an aqueous solution of $\text{CuSO}_4$ and $\text{Na}_2\text{S}_2\text{O}_3$. Different compositions of $\text{Cu}_x\text{S}$ were deposited in acidic medium (ph~3.0) for 30 min for the duration of 1-2 h photo irradiation. Results revealed that change in the ratio of copper–sulfur concentrations vary the composition of the films. Optical spectra revealed that most of the films are highly transmissive throughout the visible region and absorptive in the NIR region. Further with the increase of sulfur content, the optical absorbance edge shifts continuously from 720 to 573 nm.

Carolyn Munce et al (2007) prepared $\text{Cu}_x\text{S}$ thin films from chemical bath deposition method on glass, silicon, gold and platinum substrates. The prepared films were modified by aging the deposit under ambient conditions, annealing in air, soaking in cupric ion solution and by fixing the electrode potential. It was reported from the result that the deposited film exhibits a two layer structure with the inner layer similar in density to bulk CuS and outer less dense layer. Annealing the film in cupric ion solution converts the deposited film into a single layer. Composition of
the layer could be altered by controlling the electrode potential, which results in changes in the structure.

Cu$_x$S thin films ($x = 1.0, 1.76$ and $2.0$) were grown by solution growth technique (SGT) using thiosulfate, which acts as both complexing and sulfiding agent by Bagul et al (2007). The deposition parameters such as pH of solution, deposition time, and deposition temperature were optimized and the films were annealed in Ar atmosphere at $250^\circ$C. XRD pattern of as-deposited films shows amorphous nature and the peaks are strongly oriented along the planes due to annealing.

Ilenikhena (2008) prepared CuS thin film on glass substrate with different pH values and Ethylene Diamine-Tetra Acetate (EDTA) as complexing agent using a Chemical Bath Deposition (CBD) method. He reported that absorbance spectra of CuS film depends on the deposition of pH value and on the wavelength of radiation. The films have high absorbance for wavelengths lower than $300$nm and low absorbance for wavelength in the range $350 - 900$nm.

Sagade and Sharma (2008) have used solution growth technique to deposit Cu$_x$S ($x = 1, 1.4, \text{ and } 2$) thin films on glass substrates at room temperature (300 K). The physico-chemical properties of the films are highly influenced by the chemical composition. It was observed that the contact angle for Cu$_{1.4}$S is larger than those of Cu$_2$S and CuS thin films. Moreover film synthesized with $x=1.4$ have high surface energy. Ammonia gas sensors are fabricated by using these copper sulphide thin films with silver metal contacts. Based on the time-dependent result Cu$_x$S serve as sensor material for the detection of ammonia molecule at room temperature.

Rodriguez-Lazcano et al (2009) synthesized CuS thin films by chemical bath deposition method. The films were post treated in alternating
current air plasma for 20 min and compared with the films annealed at 300 °C. A phase transformation of Cu$_{39}$S$_{28}$ (as grown) to CuS has been observed in the measurements when the films are treated with plasma. Increase in grain size is more pronounced for the samples with thermal annealing due to temperature effects. Moreover no changes in band gap of the film were observed under the plasma action.

Mudi Xin et al (2009) coated CuS nanoplates on F: SnO$_2$ (FTO) glass substrates through a mild microwave assisted chemical bath deposition process in which copper acetate reacts with ethylenediamine tetraacetate acid disodium and thioacetamide in aqueous solution for 40 min. They reported that CuS presented the strong photo-absorption properties in the visible light region between 525 nm and 575 nm. Increasing the thickness of films results in the reduction of relative amount of insulating gaps between aggregated particle areas, and thereby, increasing conductivity.

Zhuge et al (2009) deposited amorphous Cu$_2$S thin films on ITO substrate by Successive Ion Layer Adsorption and Reaction (SILAR) method. Anionic thiosulfatocopper (I) complex ion was used as the single precursor for copper and sulfide ions, and ethylene glycol was used as the solvent ions. Formation of amorphous Cu$_2$S was due to the inhibition of the crystallization process by the solvent ethylene glycol. The amorphous structure was stable and it remains amorphous even after heat treatment at 300 °C in nitrogen.

The sodium/copper sulfide (Na/Cu$_2$S) rechargeable batteries are prepared using 1M NaCF$_3$SO$_3$-TEGDME liquid electrolyte at room temperature by Jong Seon Kim et al (2009). The curve shows a slope shape without plateaus potential region and the first discharge capacity curve of Na/Cu$_2$S cells is at 294mAh$^{-1}$ and decreases to 220mAh$^{-1}$ after 20 cycles. The discharge process can be explained by intercalation of sodium into Cu$_2$S phase without phase separation of Cu$_2$S.
Bollero et al (2009) deposited Cu$_x$S thin films of various thicknesses on soda–lime glass substrates by thermal co-evaporation of Cu and S. Result shows that lower thickness film exhibits optimum optical properties which makes it as effective solar control glazing in warm climates. It was observed that mean grain size increases with an increase in the film thickness which tends to decrease the resistivity of the film. In another work Bollero et al (2011) prepared copper sulfide (CuS) thin films with different thickness by thermal co-evaporation of the elemental constituents followed by encapsulating the films in a double glass configuration for optical characterization of the film. The studies showed that morphological and microstructural properties vary with film thickness. Annealing of the films in air and argon at a temperature 150 °C does not influence the morphological and microstructural properties, resulting in unchanged optical and electrical property that highlights the thermal stability of the films.

Yung-Tang Nien and In-Gann Chen (2009) prepared (Cu$_x$S, $x = 2$) thin film of thickness around 40nm by chemical bath deposition technique at room temperature on glass and silicon substrates from a solution containing copper complex and thiourea. From the study it was reported that as-deposited Cu$_2$S was found to convert to CuS at 200–300°C by referring to the shifts in the peaks of Raman and X-ray photoelectron spectrum. Optical transmission spectra also revealed the phase transformation of the as deposited Cu$_x$S film from Cu$_2$S to CuS at 200–300°C. Moreover Cu$_2$S films exhibit strong condensation after rapid thermal annealing at temperatures >200°C, which is believed to result from decomposition of solvents or films.

CuS, Cu$_{0.6}$Zn$_{0.4}$S and ZnS thin films were grown by successive ionic layer adsorption and reaction (SILAR) method on glass substrates at room temperature by Ali Yildirium et al (2009). Effect of annealing temperature on the crystal structure and optical band gap has been reported.
Moreover, the light effects on the electrical properties of these films have also been investigated. Using the absorption measurements, the band gap energies for CuS, Cu$_{0.6}$Zn$_{0.4}$S and ZnS thin films were found to be 2.03, 2.14 and 3.92 eV at room temperature, respectively. It was reported that current increases with increasing light intensity, and increase in the current values of CuS and Cu$_{0.6}$Zn$_{0.4}$S films have been observed for the films annealed at 400 °C. But the annealed ZnS thin film has less current values than the as-grown film.

Santheep Mathew et al (2009) synthesized copper sulfide (Cu$_x$S) particles through photochemical method from an aqueous solution containing Copper Sulfate (CuSO$_4$) and sodium thiosulfate (Na$_2$S$_2$O$_3$) of different compositions. The particles of various compositions were deposited in acidic medium (pH $\sim$3) for duration of 1-2 hr of photo irradiation. The amount of particles formed depended on the time of irradiation, about 75% of the reagents was converted into fine Cu$_x$S particles.

Anuar Kassim et al(2010) deposited copper sulphide thin films using chemical bath deposition method at various pH values and electrolyte concentrations. X-ray diffraction patterns confirmed that the deposited materials were CuS with hexagonal phase. The films deposited using 0.05 M of copper chloride and sodium thiosulfate solutions at pH 3 showed better crystallinity, uniform surface coverage and high absorption characteristics. In another report by Anuar Kassim et al (2011) the grain size and average atomic ratio of Cu/S increased when the bath temperature was increased from 55°C to 75°C. The film deposited at 75°C indicates high absorbance when compared to other bath temperatures.

Luminita Isac et al (2010) deposited Cu$_x$S thin films onto pre-heated FTO glass substrate, by ASPD technique, at temperatures in the range of 275-325°C, with pressure of carrier gas (air) at 1.2 bar. The number
of spraying sequences (nsp) was varied from 15 to 35, with 20 second breaks between two pulses with pulse duration of 10 seconds. The composition of the films is influenced by the variation of precursors’ solution composition (especially molar ratio Cu:S) and deposition temperature. Increasing the sulphur concentration in the precursors’ solution favors the mixtures in which copper-poor phase is predominant (CuS) whereas lowering the sulphur content results copper-rich phases (Cu$_2$S). The same effect was observed for the films deposited at higher deposition temperature (T = 300-325ºC).

Nourhene Kamoun Allouche et al (2010) deposited Cu$_2$S thin films on various substrates (SnO$_2$:F/glass, glass) by chemical bath deposition technique. The depositions were carried out about 32.5 min in the pH range of 9.4 to 11. XRD study shows that Cu$_2$S films exhibit better crystallite for pH = 10.2. Using the Kelvin method, the work function difference for Cu$_2$S films deposited on SnO$_2$/glass substrates at the optimum pH value was found to be equal to 145 meV.

Li Yuebin et al (2010) developed copper sulfide (CuS) nanoparticles as a new type of agent for photothermal ablation of cancer cells. CuS nanoparticles were synthesized by wet chemistry and their application in photo thermal ablation of tumor cells was tested by irradiation using a Near-Infrared (NIR) laser beam at 808 nm to elevate the temperature of aqueous solutions of CuS nanoparticles as a function of exposure time and nanoparticle concentration. CuS nanoparticle-mediated photothermal destruction was evaluated using human cervical cancer HeLa cells with respect to laser dose and nanoparticle concentration. CuS nanoparticles have an optical absorption band in the NIR range with a maximum absorbance at 900 nm. Irradiation by a NIR laser beam at 808 nm resulted in an increase in the temperature of the CuS nanoparticle aqueous solution as a function of exposure time and nanoparticle concentration.
Swarup Kumar Maji et al (2011) fabricated nanocrystalline CuS thin films using a Metal Organic Deposition Technique (MOD) from a single source precursor. Hall coefficient and Hall mobility showed linear relationship and decrease with the magnetic fields, while magneto-resistance was found to increase proportionally with the applied field. Moreover the carrier concentration and resistivity of the film were found to increase linearly with applied magnetic fields.

The effect of different mild post-annealing treatments at 270°C for 4–6 min in air, on optical, electrical, structural and chemical properties of copper sulphide (Cu$_x$S) thin films deposited at room temperature are reported by Parriera et al (2011). The as-deposited highly conductive crystalline CuS (covellite) films show high carrier concentration ($10^{22}$ cm$^{-3}$), low electrical resistivity and inconclusive p-type conduction. After mild post-annealing, these films display increasing values of resistivity with annealing time and exhibit conclusive p-type conduction. An increase of copper content in Cu$_x$S phases towards semi conductive Cu$_2$S compound with annealing time was reported, due to re-evaporation of sulphur from the films.

Ubale et al (2011) prepared nanostructured Cu$_2$S thin films using cupric acetate and sodium thiosulphate as cationic and anionic precursor, at room temperature by chemical bath deposition technique. Cu$_2$S films of different thicknesses were prepared by varying the deposition time from 9 to 24 hr. As thickness increases, the hexagonal covellite phase of CuS observed at thickness 70 nm gets converted to monoclinic chalcosite phase of Cu$_2$S. Resistivity and activation energy of the film was found to be thickness dependent. The optical band-gap energy increases from 2.48 to 2.90 eV as thickness decreases from 233 to 70 nm.

Malekar and Fulari (2011) studied the surface deformation of electrodeposited copper sulphide thin films on stainless steel substrate by
holographic interferometry technique. The work was concerned with the formation and interpretation of fringe patterns, which appears when a wave generated at some earlier time and stored in a hologram is later reconstructed by interfering with comparison wave. Furthermore, fringe spacing changes with deposition time as well as solution concentration.

Mio Chen et al (2011) fabricated patterned copper sulfide (Cu$_x$S) microstructures on Si (1 1 1) wafers by a relatively simple solution growth method using copper sulfate, ethylenediaminetetraacetate and sodium thiosulfate aqueous solutions as precursors. The Cu$_x$S particles were selectively deposited on a patterned self-assembled monolayer of 3-minopropyltriethoxysilane regions created by photolithography and high quality Cu$_x$S films have been obtained by optimizing the preparative conditions such as concentration, proportion, pH and temperature of the precursor solutions. Optical microscopy and AFM results indicated that the Cu$_x$S micro-pattern possessed high selectivity and clear edge resolution. Both SECM image and cyclic voltammograms confirmed that the Cu$_x$S film had good electrical conductivity and the apparent electron-transfer rate constant (k) in the micro-pattern of Cu$_x$S dominated surface was estimated at 0.04 cm/s.

Cu$_2$S thin films have been deposited by solution bath technique on glass substrates using copper II chloride, thiourea, TEA and ammonium hydroxide by Offiah et al (2012). The optical studies show that the films annealed at 300°C and 400°C has very high transmittance and low reflectance when compared to as-deposited sample.

2.2 SUMMARY

Cu$_2$S thin films reported previously by many researchers using different methods have been analyzed in detail. Result and discussion of their work help to gain some knowledge about Cu$_2$S material.